$WOCl_3 \cdot 2HMPA$ which was the only pure quinquevalent tungsten compound isolated was found to be 1.40 BM. This value is a little lower than the room-temperature values of most $WOCl_5^{2-}$ and $WOCl_4^-$ salts,[19] but similar to the value reported for $WOCl_3 \cdot$dipy.[6]

The reflectance spectra of $WOCl_3 \cdot 2L$ (L = $OP(C_6H_5)_3$ and HMPA) given in Table III are very similar to that of the $WOCl_5^{2-}$ ion.[21]

No attempts will be made at present to assign the bands in view of the problems associated with heavy-metal d^1 oxo species.[19,23]

As expected the WO_2Cl_2 complexes do not absorb in the visible region; however, their ultraviolet spectra (Table II) show certain similarities when allowance is made for ligand absorptions. $WO_2Cl_2 \cdot 2CH_3CN$, $WO_2Cl_2 \cdot 2DMF$, $WO_2Cl_2 \cdot 2DMSO$, and $WO_2Cl_2 \cdot 2TMSO$ are the only compounds which should not exhibit internal ligand absorption bands, so the spectra of these complexes should show bands typical of the WO_2Cl_2 group. The first low-energy transition at 34.3 kK in $WO_2Cl_2 \cdot 2CH_3CN$ is fairly weak in intensity, and since this compound is very easily hydrolyzed it is possible that this band is caused by impurity or a ligand ↔ metal transition peculiar to CH_3CN since none of the other complexes exhibits a band in this region which is not attributable to the ligand. The other two bands at 39.2 and 45.6 kK are observed, usually at slightly lower wavelengths, in all of the complexes, with the exception of the triphenylphosphine oxide, dipyridyl, and phenanthroline compounds where ligand absorptions obscure these regions. Neumann and Cook[24] observed two bands in the ultraviolet spectra of Mo(IV) solutions which were characteristic of oxo species with a Mo:Cl ratio of 1:2, and these bands occurred at similar wavelengths to those of the WO_2Cl_2 ligand species.

The internal ligand transitions are generally observed at lower frequencies in the complexes than in the free ligand. This shift is quite large for dipyridyl as has been noted before.[25]

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The Reduction of Cobalt(III) by Neptunium(V) and the Neptunium(V)–Chromium(III) Complex[1]

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The rate law for the reaction Np(V) + Co(III) = Np(VI) + Co(II), from 5 to 25° in perchloric acid–lithium perchlorate solutions of constant ionic strength, is $-d[Np(V)]/dt = k'[Np(V)][Co(III)]$ where $k' = k_0 e^{-\beta[H^+]}$. Under the same conditions, the rate law for the reaction Co(III) + Np(V)·Cr(III) = Co(II) + Np(VI) + Cr(III) is $-d[Np(V) \cdot Cr(III)]/dt = k_c'[Np(V) \cdot Cr(III)][Co(III)]$ where $k_c' = k_c''[H^+]^{-1} e^{-\beta'[H^+]}$. Presumably the exponential factor in each of these rate laws is caused by mild medium effects.

Introduction

The oxidation of the hydrated Np(V) ion to Np(VI) involves minimal changes in the primary coordination spheres of these species. The question posed is what effect will a weak complex between Np(V) and Cr(III) have, in terms of the relevant kinetic parameters, when a common reagent Co(III) is used as the oxidant? This communication presents the results obtained in such a comparative kinetic study.

Experimental Section

Reagents.—The preparation and standardization of the Np(V), perchloric acid, and lithium perchlorate solutions have been described in a previous publication.[3] Fresh stock solutions of the Np(V)·Cr(III) complex were prepared prior to use by the ion-exchange procedure previously described for the isolation of the Np(V)·Rh(III) complex.[4]

Cobaltous perchlorate was prepared from reagent grade cobaltous carbonate and perchloric acid. The perchlorate salt was recrystallized twice from perchloric acid. The crystals were then dissolved in triple-distilled water. Cobalt(III) perchlorate solutions were prepared both by electrolytic oxidation of the cobaltous perchlorate and in a few cases from the cobalt(III) carbonate complex following the procedure outlined by Hofmann-Bang and Wulf.[5]

Procedures. A. The Np(V)–Co(III) Reaction.—The molar extinction coefficient of Co(III) at 6020 A was determined as $34.5 \pm 0.1\ M^{-1}\ cm^{-1}$ in 1 *M* perchloric acid.[6] The stoichiometry of the reaction

$$Co(III) + Np(V) = Co(II) + Np(VI) \qquad (1)$$

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[1] Based on research performed under the auspices of the U. S. Atomic Energy Commission.

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[3] R. C. Thompson and J. C. Sullivan, *J. Am. Chem. Soc.*, **89**, 1096 (1967).

[4] R. K. Murmann and J. C. Sullivan, *Inorg. Chem.*, **6**, 892 (1967).

[5] N. Hofmann-Bang and I. Wulf, *Acta Chem. Scand.*, **9**, 1230 (1955).

[6] This is in excellent agreement with the value of 34.76 $M^{-1}\ cm^{-1}$ determined by D. W. Weiser, Ph.D. Dissertation, University of Chicago, June 1956.

Table I

$[H^+]$ and Temperature Dependencies of k' [a]

5°		10°		17°		25°	
$[H^+]$, M	k', M^{-1} sec^{-1}	$[H^+]$, M	k', M^{-1} sec^{-1}	$[H^+]$, M	k', M^{-1} sec^{-1}	$[H^+]$, M	k', M^{-1} sec^{-1}
2.10	68.4 ± 3.6	2.10	90.3 ± 1.2	2.10	169 ± 5	2.10	300 ± 3
1.70	66.2 ± 3.0	1.68	94.7 ± 0.5	1.70	164 ± 2	1.68	306 ± 1
1.28	64.8 ± 1.8	1.27	95.8 ± 1.0	1.28	156 ± 4	1.27	318 ± 9
0.89	65.4 ± 2.1	0.86	91.6 ± 5.3	0.88	166 ± 4	0.87	308 ± 1
0.49	67.3 ± 3.5	0.46	101 ± 1	0.47	176 ± 4	0.46	330 ± 6
0.29	74.4 ± 5.3	0.26	110 ± 4	0.28	202 ± 2	0.26	401 ± 2

[a] $[\mathrm{Np(V)}]_0 = (2.23\text{–}9.42) \times 10^{-4}\ M$; $[\mathrm{Co(III)}]_0 = (1.60\text{–}7.30) \times 10^{-4}\ M$; $\mu = 2.10$ maintained with $LiClO_4$. Entries are the average values determined for two to six independent observations. The listed uncertainties are standard deviations.

was determined using this value for ϵ(Co(III)) plus the previously determined value of ϵ(Np(V)) at 9805 A. The ratio of [Co(III) (reacted)]/[Np(V) (reacted)] = 1.008 ± 0.005.

For the kinetic runs all of the reagents, except the Co(III), were pipetted into 2- or 5-cm absorption cells. The cell was placed in the thermostated compartment of the Cary Model 14 MR spectrophotometer and an aliquot of the Co(III)—from a stock solution thermostated at the working temperature—was introduced into the cell. The absorptivity at the Np(V) peak was recorded as a function of time. The $[H^+]$ of the reaction mixture was determined by titration after completion of the reaction.

The first observation was generally made within 10 sec after mixing and the reaction was followed to within 95–99% of completion. Values reported for k' were obtained from a least-squares adjustment of the data (20–30 OD, t data points per experiment) for the functional form previously described.[3]

B. The Np(V)·Cr(III)–Co(III) Reaction.—The stoichiometry of the reaction

$$\mathrm{Np(V)\cdot Cr(III) + Co(III) = Np(VI) + Co(II) + Cr(III)} \quad (2)$$

was determined spectrophotometrically by treating excess Co(III) with the complex in 2 M $HClO_4$ at 25° and measuring the decrease in absorptivity at 6020 A. The ratio of [Co(III) (consumed)]/[complex consumed] = 0.97. The amount of complex initially present was determined using the absorptivity of the complex at 9935 A where $A = 228\ M^{-1}\ \mathrm{cm}^{-1}$.[7]

The chromium(III) product in reaction 2 was identified as $Cr(H_2O)_6^{3+}$ rather than a more highly charged polynuclear species. A spent reaction mixture was eluted from a Dowex-50 (100–200 mesh) column with 4 M $HClO_4$. Any +4 or more highly charged polynuclear species of Cr(III) would not be eluted by this procedure. The eluent was heated to dryness and dissolved in base, and the Cr(III) present was converted to Cr(VI) with H_2O_2. The Cr(VI) concentration was determined spectrophotometrically. An aliquot of the complex solution was treated in the same manner with the omission of the column separation. The ratio of the Cr(VI) formed in the first procedure to that formed in the second was 0.97.

Essentially the same procedures were employed in the kinetic experiments as described above. The absorption peak of the complex at 9935 A was used to monitor the reaction. The rate constants for the most part were calculated as described above although in some cases pseudo-first-order kinetics were observed since between a 5- and 12-fold excess of Co(III) was used for convenience. Appropriate blank experiments indicated that the reaction time in all of the rate studies was rapid compared to the rate of the reduction of Co(III) by H_2O.

Results

A. Np(V)–Co(III) Reaction.—The observed OD, t data points were reproduced by the two parameters to $\leq$0.003 OD unit. The precision indices assigned to the rate parameter k' ranged from 0.2 to 1%. The reproducibility of replicate runs, as is evident from the data in Table I, was between 1 and 6%.

The majority of the experiments were carried out with Co(III) that had been prepared electrolytically. From experiments in which the Co(III) was prepared *in situ* there was no indication that the method of preparation had an effect on the reaction rate. For example, in 2 M $HClO_4$ at 25° values determined for the second-order rate parameter (in M^{-1} sec^{-1}) were 300 ± 3 and 308 ± 9 for sets using electrolytically and chemically prepared Co(III), respectively.

In view of the previous comments, it is not unexpected that Co(II) has no apparent effect on the rate. At 5°, in 2.1 M $HClO_4$ the second-order rate parameter had the value 72.1 ± 0.8 M^{-1} sec^{-1} in a set of experiments with an initial Co(II) concentration of 0.036 M. This is to be compared to the value of 68.4 ± 3.6 without added initial Co(II).

The variation of the rate of reaction with change in $[H^+]$ and temperature is summarized in Table I.

A limited number of observations on the effect of changing ionic strength are summarized in Table II.

Table II

Effect of Ionic Strength on the Np(V)–Co(III) Reaction

5° [a]		25° [b]	
μ	k', M^{-1} sec^{-1}	μ	k', M^{-1} sec^{-1}
0.49	32.2 ± 1.5	0.46	176 ± 3
1.09	41.4 ± 1.2	1.06	232 ± 4
2.10	67.3 ± 3.5	2.10	330 ± 6

[a] $[H^+] = 0.49\ M$; $[\mathrm{Np(V)}]_0 = 4.43 \times 10^{-4}\ M$; $[\mathrm{Co(III)}]_0 = (3.66\text{–}3.93) \times 10^{-4}\ M$. [b] $[H^+] = 0.46\ M$; $[\mathrm{Np(V)}]_0 = 4.50 \times 10^{-4}\ M$; $[\mathrm{Co(III)}]_0 = (2.97\text{–}3.27) \times 10^{-4}\ M$.

At 10°, in 2.10 M $HClO_4$ values were determined for k' of 94.7 ± 2.8 and 95.6 ± 2.6 M^{-1} sec^{-1} with initial concentrations of 10^{-3} M H_2SO_4 and HCl, respectively. For the same acidity, at 17° values were determined for k' of 169 ± 2 and 172 ± 2 with initial concentrations of 10^{-3} M Na_2HPO_4 and NaF, respectively. Comparison with the values in Table I indicates that there was no catalysis by these added anions.

B. The Np(V)·Cr(III)–Co(III) Reaction.—The standard deviations in the rate parameter k_c' ranged from 0.9 to 3.2%. The reproducibility of replicate runs was between 1 and 8%.

The variation of the rate of the reaction as a func-

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(7) J. C. Sullivan, *J. Am. Chem. Soc.*, **84**, 4256 (1962).

TABLE III

$[H^+]$ AND TEMPERATURE DEPENDENCIES OF k_c' [a]

5°		10°		17°		25°	
$[H^+]$, M	k_c', M^{-1} sec^{-1}	$[H^+]$, M	k_c', M^{-1} sec^{-1}	$[H^+]$, M	k_c', M^{-1} sec^{-1}	$[H^+]$, M	k_c', M^{-1} sec^{-1}
1.99	0.109 ± 0.002	2.08	0.203 ± 0.002	2.06	0.466 ± 0.009	2.05	1.08 ± 0.08
1.51	0.155 ± 0.002	1.55	0.280 ± 0.004	1.43	0.650 ± 0.016	1.48	1.60 ± 0.02
1.02	0.223 ± 0.001	1.11	0.420 ± 0.001	1.08	0.883 ± 0.002	1.02	2.28 ± 0.17
0.86	0.283 ± 0.001	0.84	0.546 ± 0.009	0.73	1.46 ± 0.03	0.67	4.07 ± 0.20
0.51	0.471 ± 0.003	0.64	0.661 ± 0.018	0.61	1.66 ± 0.01	0.46	4.98 ± 0.06

[a] $[Np(V)\cdot Cr(III)]_0 = 5.04 \times 10^{-4}$ to $1.04 \times 10^{-3}\ M$; $[Co(III)]_0 = (3.49\text{–}9.80) \times 10^{-3}\ M$; $\mu = 2.10\ M$ maintained with $LiClO_4$. Entries are the average values determined for two to six independent observations. The listed uncertainties are the average deviations.

tion of $[H^+]$ and temperature is summarized in Table III.

At 25° in 2.02 M $HClO_4$, the value $k_c' = 1.10\ M^{-1}$ sec^{-1} was determined with an initial concentration of $10^{-3}\ M$ NaF. The corresponding value in Table III indicates that there was no detectable catalysis by HF.

Discussion

A. The Np(V)–Co(III) Reaction.—The empirical dependence of the rate with variation in hydrogen ion concentration expressed in the usual manner is

$$k' = k[H^+]^n$$

where $n = -0.064 \pm 0.021$, -0.090 ± 0.020, -0.044 ± 0.022, and -0.112 ± 0.023 at 5, 10, 17, and 25°, respectively. This result indicates that the activated complex composed of one Co(III) and one Np(V) molecule (with an undetermined number of molecules of H_2O) provides the dominant path for the reaction. The small, but empirically significant, deviation of n from zero can reasonably be justified in terms of variation of activity coefficient ratios with change in solution composition. This interpretation is not inconsistent with the data presented in Table II. In terms of such a Harned-type correction factor

$$k' = k_0 e^{-[\beta H^+]}$$

the values computed for the rate parameter k_0 are 355 ± 16, 176 ± 6, 104 ± 4, and 73.1 ± 2.8 M^{-1} sec^{-1} at 25, 17, 10, and 5°, respectively. At the same temperatures values of β are 0.09 ± 0.03, 0.03 ± 0.02, 0.09 ± 0.03, and 0.06 ± 0.02.

The energy of activation was calculated to be 12.9 ± 0.6 kcal/mole and $\Delta S^* = -5 \pm 3$ eu.

As Sutin has pointed out,[8] three of the four cases where the simplified formulas of the Marcus theory do not predict the observed value of the rate constant involve Co(III) species as one of the reactants. This turns out to be also true for the reaction under consideration. The calculations use the reduced form of the Marcus equations[9]

$$k_{12} = (k_1 k_2 K_{12} f)^{1/2}$$

$$\log f = (\log K_{12})^2/4 \log (k_1 k_2/Z^2)$$

where K_{12} is the equilibrium constant for reaction 1, and k_1 and k_2 are the specific rate constants for the isotopic exchange reactions between Np(V)–Np(VI) and Co(II)–Co(III), respectively. The value calculated for k_{12} is $2.8 \times 10^6\ M^{-1}$ sec^{-1} [10] at 25°. This is to be compared to the observed value of $3.35 \times 10^2\ M^{-1}$ sec^{-1}.

The discrepancy between calculated and observed values may arise from a number of factors[11] including the formation of an inner-sphere activated complex in the reaction. The small value calculated for ΔS^* may be used to suggest that an outer-sphere activated complex is attained in the Np(V)–Co(III) system and that some of the other points previously discussed by Dulz and Sutin may preclude the application of the theory for this reaction.

B. The Np(V)·Cr(III)–Co(III) Reaction.—The empirical dependence of k_c' with variation in the $[H^+]$ was analyzed according to the expression

$$k_c' = k_c[H^+]^n$$

where $n = 1.08 \pm 0.02$, -1.13 ± 0.02, -1.07 ± 0.03, and -1.08 ± 0.05 at 5, 10, 17, and 25°, respectively. This result indicates that the activated complex composed of one Co(III), one Np(V)·Cr(III), and one less than the usual number of H^+ (with an undetermined number of H_2O molecules) provides the dominant path for this reaction.

The small deviation from inverse first-order $[H^+]$ dependence is interpreted as a variation of activity coefficient ratios with change in the solution composition. In terms of a Harned-type correction factor

$$k_c' = \frac{k_c'' e^{-\beta'[H^+]}}{[H^+]}$$

the values computed for the rate parameter k_c'' are 2.33 ± 0.05, 0.951 ± 0.009, 0.463 ± 0.004, and 0.233 ± 0.005 sec^{-1} at 25, 17, 10, and 5°, respectively. At the same temperature, values of β' are 0.07 ± 0.08, 0.05 ± 0.05, 0.31 ± 0.05, and 0.14 ± 0.04.

The energy of activation was calculated to be 18.2 ± 0.7 kcal/mole and $\Delta S^* = 2 \pm 3$ eu.

The complex formed between Np(V) and Cr(III) is weak, in the thermodynamic sense, since the equilibrium quotient at 25° is 2.62 ± 0.48 and the enthalpy of the reaction is -3.3 ± 0.6 kcal. However, since the rate of decomposition of the complex at 25° is (2.34 ± 0.08)

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(8) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 164 (1966).

(9) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

(10) Pertinent values for this calculation are: Co(II)–Co(III) couple −1.84 v (W. H. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952); Np(V)–Np(VI) couple, −1.13 v (A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, **66**, 1065 (1962)); Co(II)–Co(III) exchange reaction, $k = 4.02\ M^{-1}$ sec^{-1} (H. S. Habib and J. P. Hunt, *J. Am. Chem. Soc.*, **88**, 1668 (1966)); Np(V)–Np(VI) exchange reaction, $k = 1.1 \times 10^2\ M^{-1}$ sec^{-1} (D. Cohen, J. C. Sullivan, and J. C. Hindman, *ibid.*, **76**, 352 (1954)).

(11) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

$\times\ 10^{-6}$ sec^{-1}, there is negligible dissociation of this species during the course of the redox reaction.[7]

The most significant difference between the kinetic description of this system, compared to the reaction between the aquated Np(V) and Co(III), is the change in the empirical form of the rate law. An *a posteriori* rationale of the observations would invoke the hydrolytic preequilibrium of one of the reactants followed by the obvious rate-determining step when the Np(V)·Cr(III) complex is the reductant. In this context, *i.e.*, reduction of the net formal charge of the activated complex providing a preferred kinetic path, it is of interest to note that no system has been reported for the actinide ions with formal charge greater than +6.[12]

A calculation of the predicted rate constant k_c'' using the formulas of the Marcus theory is not feasible on the basis of at least two considerations. First, even if the reaction does meet all of the criteria necessary for such a calculation (such as outer-sphere mechanism, favorable interaction between redox orbitals, etc.), the data presented do not preclude a path in which the Co(III) attacks the complex at the Cr(III) site

$$\mathrm{Co(III)}\text{—}\mathrm{Cr(III)\cdot Np(V)} \longrightarrow \mathrm{Co(II)} + \mathrm{Cr(IV)\cdot Np(V)}$$

Whatever the fate of the Cr(IV) in such a scheme (*i.e.*, direct electron exchange between the Cr(IV) and the Np(V) could occur, or dissociation of the complex followed by subsequent oxidation of the Np(V) and reduction of the Cr(IV)), the over-all stoichiometry and kinetics would fit the data. The data do preclude the formation of Cr(VI) in the reaction,[13] as would be expected from the slow rate of the oxidation of Cr(III) to Cr(VI) by Co(III).[14]

Second, the electron-transfer reaction between Np(VI) and Np(V)·Cr(III) has not been studied. The present work does indicate that this rate must be much slower than the Np(VI)–Np(V) exchange reaction,[10] since second-order kinetics were observed with respect to the metal ions.

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[12] T. W. Newton and F. B. Baker, Paper O-30, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[13] In 2 *M* $HClO_4$ at 25° there was no detectable oxidation of the complex (*ca.* 10^{-3} *M*) by 0.01 *M* Cr(VI) after several hours.

[14] J. B. Kirwin, P. J. Proll, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **60**, 119 (1964).

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Ion Pairing and Interionic Distances in Solution for Paramagnetic Complexes from Proton Magnetic Resonance Shifts[1a]

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The proton magnetic resonance spectra have been observed for deuteriochloroform solutions of the Co(II) and Ni(II) complexes $[(C_6H_5)_4As][(C_6H_5)_3PM^{II}I_3]$. For the cobalt complex, large cation chemical shifts arise from a dipolar (pseudo-contact) interaction between ions in an ion pair. Several models for the ion pair are postulated, and their relative dipolar shifts calculated. Best agreement between the calculated and observed shift ratios was obtained with a model in which the cation lies along the C_3 axis of the anion, with a cation C_2 axis coincident with the unique anion axis and with the two ions separated by 9.0 ± 0.8 A. Certain other reasonable models give roughly similar results and may contribute to some extent. The validity of this method of analysis is supported both by the precision of the three estimates and by the relative line widths for the proton resonance peaks of the cation. The relative advantages of studying ion pairing from dipolar shifts and line widths are discussed.

Introduction

It has recently been shown[2] that the large proton chemical shifts observed for the diamagnetic cation of an ionic, paramagnetic complex in solution are the result of a dipolar nucleus–electron interaction[3] between ions in an ion pair. From the pattern of observed isotropic shifts it has also been possible to estimate the interionic distance.[2b] Since then, such dipolar shifts have been observed in some other systems[4,5] where they were also related to ion association.

This dipolar or pseudo-contact interaction[3] arises in a system where the metal ion possesses significant magnetic anisotropy and results in proton resonance shifts from the positions observed in a similar diamagnetic system. For a given complex, the magnitude of the fractional dipolar shift for any proton depends only on the g tensor, certain physical constants for the electron and proton, the temperature, and a geometric factor which relates the relative orientation of the proton with respect to the g tensor,[3] such that the relative dipolar shifts for a given complex are simply proportional to their geometric factors.[2b] Dipolar shifts for a cation vanish if it does not maintain a preferred orientation

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